TRANSPORT PHENOMENA IN GLASS TECHNOLOGY (REVIEW)

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The role of transport phenomena and technological processes in glass production is noted. The salient features of a change in transport phenomena accompanying changes of the temperature and chemical composition of glasses for fused and solidified states of glass are examined. The interrelationship of transport phenomenon is also examined. Glass forming melts possess a high viscosity. The latter has a large effect on transport phenomena associated with particle motion; this effect is also expressed by definite relations. The results of experimental and theoretical investigations, presented in the scientific and technical literature, are discussed from structural and technological standpoints.

Transport phenomena are encountered in every technological process. They include processes where mass or energy transfer occurs from certain particles of a nonuniform material system to other particles in the system. It is usually assumed that the system consists of one phase but its properties are nonuniform.

If a material or energy gradient is present in a system or body, then transport of the corresponding kinetic units (atoms, ions, phonons, and so forth) occurs:

$$F = -K \, d\Phi/dx,$$

where F is the flux of the kinetic units determining some property, K is the coefficient of proportionality, and $d\Phi/dx$ is the gradient of the determining characteristics: flow velocity, temperature, concentration, electric potential.

The most important types of transport are transport of impulse or momentum, heat, mass, and electric charge.

During heat conduction, thermal energy is transferred from particles with higher energy to particles with lower energy.

When regions with different chemical potentials are present (this difference arises, as a rule, because of a concentration difference), mass transfer occurs as a result of diffusion. A special limiting case of diffusion is self-diffusion, which is associated with disordered displacement as a result of the thermal motion of molecules, atoms, or ions within a phase with uniform properties.

During electric conduction, electric charge is transferred as a result of a difference in the electric potentials.

Transport phenomena play an important role in the technological processes involved in the production of glass articles, starting with the process of founding glass and ending with processes involved in working articles and in the interaction with the environment when glass articles are used.

In what follows, the characteristic features of transport phenomena, predominately in the high-temperature processes of glass technology, are examined. Predominantly domestic review literature containing many references to the original works, including those of foreign authors, is used.

It should be noted that the authors of [1] analyzed, using the SciGlass system, the investigation of the properties of glass over the period 1976 – 2001. It was found that over this time the number of investigations concerning transport phenomena (including dielectric properties) comprised 18.3% of the total number of investigations concerning the properties of glasses. The largest number of investigations concerned viscosity (5.7%) and electric conductivity (9.0%). Evidently, this can be explained by the importance of these properties in practice.

Transport phenomena are all similar to one another [2, 3]. In addition, there also exists a deep analogy between the mechanisms of the phenomena resulting in displacement of particles and the mechanisms of momentum transfer, which determines the resistance to particle motion. It should be noted that the principles of similarity and analogy concerning true heat conduction refer to the low-temperature range in the absence of radiation. In this case the heat flux, by analogy with diffusing and charged particles, is regarded as a flux of quasiparticles — phonons, which arises as result of thermal oscillations of a group (or a system) of atoms (ions) which are bound together. Radiation plays an increas-

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ingly larger role at high temperatures, for example, in glass above 200°C. Here, the principles of similarity and analogy with other transport phenomena are not satisfied.

Transport phenomena will be examined predominantly for the most widely used silicate glasses. For this reason, we shall briefly note the structural features of the glassy state, including the fused state, since these features determine the specific nature of transport phenomena.

The main feature of glassy silicates is the presence of a continuous and three-dimensional silicon-oxygen framework with a random arrangement of modifier cations in the voids within the framework. A complex and silicate glass is a non-uniform chemical compound of alumina with other oxides. It possesses a specific, continuous (in three dimensions), asymmetric structure. Figure 1 displays schematically the structure of sodium-calcium-silicate glass. The ions R^+ and R^{2+} satisfy the following conditions: each ion R^+ must be located near one non-bridge oxygen ion and each ion R^{2+} must located near two non-bridge ions. The presence of alkali-earth metal ions promotes structural ordering of the network. Since the ions R^{2+} are more strongly bound with the framework, they are less mobile. When more mobile alkali ions are replaced by less mobile doubly charged alkali-earth ions the mobility of the modifier ions in the glass structure decreases, which influences transport phenomena.

These features leave an imprint on the fused state. The complex silicon-oxygen framework $[Si_mO_n]$, acquiring a high mobility, partially decomposes on melting not into separate definite anions characteristic for typical salts but into diverse and very complex ions with variable structure. The interrelationship of these anions with the modifying cations becomes weaker; the latter acquire a higher mobility compared with the complex silicon-oxygen anions. Thus, these anions, forming a three-dimensional framework, are determining for the viscosity of glasses, and the more mobile cations are determining for diffusion and electric conduction.

Viscosity. The viscosity of glasses at different temperatures characterizes the specific nature of the glassy state and is a determining structural and technological property. The range of the measured values of the viscosity of glasses is unusually wide. As a rule, it covers 11 orders of magnitude and sometimes much larger. The viscosity determines the capability of a body to undergo viscous (irreversible) deformation or the degree of resistance to this deformation. In its simplest form viscosity is related with shear deformation.

There are a large number of published works on viscosity. A significant fraction of these works is systematized in the review monograph [4]. Information on viscosity is also presented in other monographs [5], textbooks, and learning aids.

There are several tens of methods for measuring the viscosity of glass. Methods based on measurements of the resistance to which a body immersed in melt is subjected as the body rotates are most widely used for studying low-viscosity melts. High viscosities are most often measured according to the rate of stretching of a glass filament under a prescribed
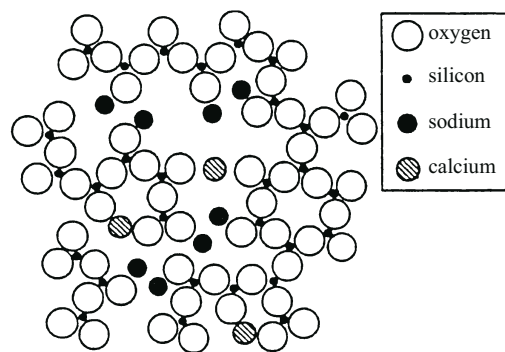

Fig. 1. Two-dimensional structural scheme of sodium-calcium-silicate glasses.

load. Methods for measuring viscosity are described in detail in the photograph [5]. Extensive material on the experimental values of the viscosity of glass for different glass-forming systems is presented in [6].

The kinetic model of glass formation shows that the temperature dependence of the viscosity is the main factor determining the ease of glass formation for a particular melt. Glasses form most easily in two cases:

the melting temperature of the crystalline phase corresponds to a very high viscosity of the melt;

the viscosity grows very rapidly as temperature decreases.

The change in the viscosity of normal liquids with a change in temperature is expressed by Ya. I. Frenkel's theoretical equation:

$$\eta = A \exp (E_\eta /RT),$$

where A is a constant coefficient, E_η is the activation energy of viscous flow, R is the universal gas constant, and T is the absolute temperature.

The applicability of Frenkel's equation to high-viscosity liquids is limited to a narrow temperature range. A number of equations, satisfactorily describing the temperature dependence of the viscosity over a wide temperature range, have been proposed for glass-forming melts [4, 5].

The high viscosity of glass-forming melts is due to the nature of the forces acting between atoms. For these melts the spatial silicon-oxygen framework has the determining effect on the viscosity. The quantity E_η in them is large and exhibits a complicated temperature dependence.

There are a number of innovative theoretical works devoted to the development of various models of the viscous flow glasses. A quite complete review of these investigations is given in [4, 7].

Viscosity is very important in the technological processes involved in the production of glass and glass articles. The character of the change in the viscosity of glass as temperature changes serves as a basis for determining the temperature regimes for founding, formation, and heat treatment.

Of all the physical and chemical properties of glasses, the viscosity depends especially strongly on the chemical composition of glass. Oxides which increase the viscosity of glass are SiO_2, Al_2O_3, and ZrO_2 and oxides which lower the viscosity are Na_2O, K_2O, Li_2O, PbO, and BaO. Often, especially at high temperatures, ZnO decreases the viscosity. Magnesium oxide increases the viscosity of glass but much less than, for example, Al_2O_3. B_2O_3 and CaO have a very strong effect on the viscosity of glass. Boron anhydride significantly lowers the viscosity of glass at high temperatures. At low temperatures and up to approximately 15% B_2O_3, the viscosity of glasses increases and decreases only with a further increase of the B_2O_3 content. Calcium oxide at low temperatures increases the viscosity of glass; at high temperatures and for CaO content up to approximately 11% the viscosity of glass decreases, and with a further increase of the CaO content the viscosity increases. The viscosity of glass at high temperatures increases when CaO is replaced with MgO. When estimating the effect of the chemical composition of glass on its viscosity, the character of the replacement of one oxide by another must be taken into account. The character of the dependence of the viscosity of silicate glasses on the composition and temperature is described in detail in the monograph [4] and the handbook [6].

For technological purposes, it is often necessary to make a rapid estimate of the effect of the chemical composition of glass on its viscosity at different temperatures. In this connection, various methods for calculating the viscosity of glass according to its chemical composition have been developed. These methods are reviewed and presented in detail in [4, 8, 9]. The best-known methods for calculating viscosity are those developed by G. Gehlhoff and M. Thomas, M. V. Okhotin for the glasses $Na_2O - CaO - MgO - Al_2O_3 - SiO_2$, V. T. Slavyanek for $(K, Na)_2O - PbO - SiO_2$, and O. V. Mazurin, N. I. Tret'yakov, and T. V. Shvaiko-Shvaikovskii (MTSh) for $Na_2O - RO - SiO_2$.

All technological processes in founding, formation, and annealing are associated with definite viscosity ranges. This is reflected in the existing technological scales of viscosity [4, 5]. Characteristic points of viscosity are indicated on the technological scales of viscosity (Pa · sec): the liquidus temperature (about 10^2); Littleton's point, determined as the onset of elongation of a glass filament under its own mass ($10^{6.6}$); the softening temperature T_f (about 10^8); dilatometric temperature of deformation (about 10^{10}); vitrification temperature T_g (about $10^{12} - 10^{12.3}$); the upper and lower annealing temperatures (about 10^{12} and $10^{13.5}$). For viscosity above $10^{13.5}$ Pa · sec, glass is in solid brittle state.

Founding (silicate and glass formation), fining, and homogenization of glass mass occur at temperatures above the liquidus point. The homogenization and fining processes proceed actively with low values of the viscosity (less than about 10^2 Pa · sec).

The temperature-viscosity intervals of formation are different for different methods. Glass pouring and shaping processes are characterized by the shortest intervals (about $10^2 - 10^{5.5}$ Pa · sec). Blowing and rolling are in the viscosity range about $10^2 - 10^7$ Pa · sec. Drawing and pressing occur at viscosities up to about 10^8 Pa · sec. The characteristics and conditions of the formation process and the production characteristics of glasses are reflected in the review [10]. The solidification rate of glass, characterized by the change of viscosity in time, is determining for the formation of glass articles. The works performed by different investigators in this direction are reflected in the review articles [11, 12].

Generalizing the results of many works, it can be asserted that the rate of processes occurring in glass-forming systems is proportional to their viscosity: inverse proportionality holds for the rates of glass formation processes during founding and annealing and direct proportionality holds for formation processes.

The high viscosity of glass-forming melts is the reason for the appearance of nonequilibrium states during rapid cooling. This is due to the manifestation of viscoelasticity, which depends on the rate of application of an external action and can occur in a wide range of values of the viscosity. For glass-forming melts, this is the region of the transition into the glassy state ($\eta = 10^8 - 10^{13.5}$ Pa · sec). When glass formation occurs as a result of nonuniform cooling and rapid application of a load, internal stresses appear in the glass. The glass is annealed to remove the stresses; annealing is limited to viscosity $10^{12} - 10^{13.5}$ Pa · sec. Conversely, during annealing, compressive stresses are produced and "frozen" in the surface layer, which makes glass articles much stronger. Questions associated with these processes are discussed in [8, 13].
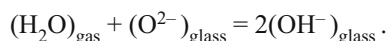
Diffusion. Spontaneous equalization of concentration — diffusion — is caused by a random walk of the defusing particles. Diverse diffusion processes occur in the glass technology: self- and heterodiffusion of ions, ion exchange on contact of glass with solutions and melts, dissolution, release of gases in glasses, and so forth. For heterogeneous chemical interactions, the limiting stage in the process is, as a rule, diffusion with the initial substances brought into the reaction zone and the products of the reaction removed into the volume of one of the phases.

The mechanism of diffusion is different for gaseous, solid, and liquid states of matter. The main theoretical ideas concerning the character of diffusion in various media, predominately in solids and liquids, are contained in the works of Ya. I. Frenkel and P. P. Kobeko and in the monograph [3]. Further elaboration of theoretical ideas about the mechanisms of diffusion in glasses and glass forming melts with contact ion exchange as well as a review of the experimental results are given in [14, 15]. The experimental results on the diffusion of ions in glasses with different composition are systematized in the handbook [6]. The results of investigations of mass transfer in the system glass-tin in application to the production of sheet glass by the float process are presented in [16, 17].

Diffusion of intrinsic and extrinsic ions in a constant electric field, specifically, with nonuniform surface coloration of a continuous ribbon of heat-polished glass, is of great importance for obtaining surface-colored and hardened technical glasses.

Diffusion phenomena with the participation of melts are important for glass technology.

Diffusion of dissolved gases determines the processes which equalize the gas concentration in melt or between the melt and the atmosphere in the furnace (saturation of melt by gas; decrease of supersaturation; bubble formation, growth, and dissolution). The questions concerning the interaction of different gases with melts are generalized in the review monographs [18, 19]. The start of fining is also based on the diffusion of gases from melt into bubbles, which grow and become more buoyant. The diffusion of gases dissolved in glass has been studied quite completely. Detailed investigations have been performed only for helium and water. The dissolution of water in glass melts is associated with the chemical interaction of water vapor in the gas medium and oxygen anions in the melt according to the reaction

$$(H_2O)_{gas} + (O^{2-})_{glass} = 2(OH^-)_{glass}.$$

OH groups form on the surface and diffuse into the bulk of the melt. Intensification of H_2O diffusion has been observed at high temperatures with increasing content of modifier ions in sodium-silicate and sodium-calcium-silicate glasses [18, 19]. By analogy with H_2O and He the diffusion of N_2, O_2, CO_2, and SO_2 also increases with increasing content of the modifier ions. Still, the dependence of the diffusion coefficient on temperature is stronger than the dependence on the composition.

Figure 2 displays generalized data obtained by different authors on the temperature dependence of the coefficients of diffusion of gases for sodium-calcium-silicate glasses [19]. The diffusion coefficients increase with temperature and as the atoms or molecules of the diffusing gas become smaller. The difference of the diffusion coefficients for different gases at low temperatures is greater than at high temperatures. Investigations of the diffusion of oxygen and reducing gases are presented in [20, 21].

A number of investigations have established that the solubility of gas and the gas permeability of melt are directly related with diffusion [18, 19]:

$$P = \Delta CD,$$

where P is the solubility of the gas, ΔC is the difference of the saturation and actual concentrations, and D is the diffusion coefficient, which ultimately determines the size of bubbles and the composition of the gases in them.

The solubility of gases forming bubbles during glassmaking is different. The gases O_2, H_2O, CO_2, and SO_2 dissolve well in glass and N_2 dissolves poorly. The solubility of gases in glass has been studied at 1000°C with a prescribed decrease of bubbles size taking account of the values of the
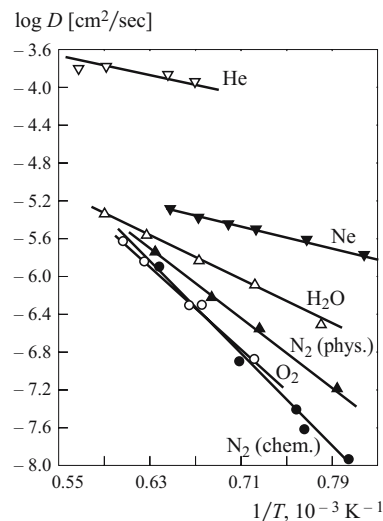

Fig. 2. Temperature dependence of the diffusion coefficients in sodium-calcium-silicate glasses.

diffusion coefficients [19]. According to experimental data and the corresponding calculations, the time required to change the bubble size, depending on the type of gas, changed in the following ratio:

$$O_2 : CO_2 : N_2 = 1 : 10^2 : 10^4.$$

This means that the desorption of gases with high chemical solubility in glass occurs comparatively rapidly and can make a large contribution to fining and, first and foremost, for small bubbles. This is the basis of the action of fining agents — oxygen and sulfates.

Diffusion phenomena where solids interact with melts are most characteristically manifested when glass melts come into contact with dissolving grains of SiO_2 (at the stage of glass formation) and with refractory materials. It should be noted that validated theoretical models of convective diffusion transport have been developed mainly for low-viscosity liquids, and in the monograph [2] it is underscored that diffusion kinetics must be studied in high-viscosity liquids, specifically, in melts. Some questions concerning diffusion phenomena with the participation of glass-forming melts are examined in the review monograph [19]. Diffusion kinetics with the interaction of corundum refractories with a glass mass is described in [22].

The characteristic features of diffusion kinetics accompanying the interaction of a glass mass with refractory materials are presented in Fig. 3. Figure 3a displays the motion of a melt and the velocity distribution in the flow of glass mass relative to a stationary refractory wall parallel to the y axis (production flow). As one can see, the flow velocity increases from zero (at the surface of the refractory) up to definite values within the hydrodynamic layer. Diffusion occurs in a direction perpendicular to the direction of motion of the glass mass, i.e., along the x axis. The main ion diffusion process occurs in a thin diffusion layer, and convective diffusion occurs outside this layer — in the hydrodynamic layer. Ge-
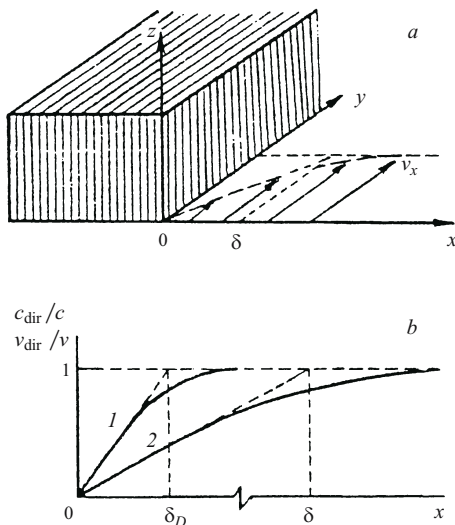
Fig. 3. Diffusion kinetics during the motion and interaction of a glass mass with refractory masonry: *a*) diagram showing the motion of the melt and velocity distribution in the flow of glass mass during convective diffusion; *b*) character of the variation of the Al_2O_3 concentration (*1*) and the velocity of melt (*2*) in the direction of diffusion flow.

neralized dependences of the variation of the reduced concentrations of the refractory substance (Al_2O_3) and the velocity of the glass mass are presented in Fig. 3*b*. It should be noted that the phenomena examined are secondary. First and foremost, formation of a diffusion layer occurs as a result of chemical interactions, concentration gradients, and surface forces.

The experimental results attest to the diffusion character of the interaction of refractories with glass mass; the diffusion coefficients of Al^{3+} ions for corundum refractories are $10^{-11} - 10^{-12}$ m²/sec.

Diffusion phenomena occurring when glasses come into contact with salt melts during ion-exchange hardening of glasses have been analyzed in detail in the reviews [14, 15].

Electric conduction. The mobility of ions, specifically, metal cations, in glassy solids is much higher than in crystals with a regular crystal lattice. The mobility of modifier cations is many times higher than that of glass-forming ions (silicon-oxygen anions) at all temperatures. Measurements of the ion transfer numbers in glass show that glasses are cationic unipolar conductors, i.e., current transfer through them occurs by means of only cations, predominately alkali cations; large silicon-oxygen anions practically do not participate in current transfer because of their immobility in solid glasses and low mobility in melts. The character of ion mobility in solid glasses and melts is due to the distorted structure of the silicon-oxygen framework and the statistical arrangement of cations in the empty spaces of the framework. Consequently, glasses contain many positions with low energy barriers for the motion of ions; high energy barriers are also present, but the average heights of the energy barriers in glasses are appreciably lower than in crystals.

A measure of the electrical conductivity is the specific volume conductivity, which is related with the specific volume electric resistance by the relation

$$\chi = 1/\rho_e .$$

The dielectric characteristics of glasses also determine the electric conductivity. Silicate glasses at temperatures below T_g are dielectrics. When a dielectric is placed in an electric field, in general, two processes occur simultaneously: movement of free charges in the direction of the poles of the field (electric conduction) and partial elastic displacement of bound charges (electrons or ions), which gives rise to local spatial redistribution of charge, i.e., polarization. The polarization of a dielectric is accompanied by energy losses, which results in heating of the glass. The higher the electric conductivity of glasses, the higher their permittivity and dielectric losses, which also increase with temperature, are. Quartz glass exhibits the lowest dielectric losses and permittivity.

Investigations of the electric conductivity of solid and fused glasses and the use of the results in industry are subjects of a substantial number of works, which are generalized and systematized in the monograph [23], collected works, and textbooks. In addition, extensive material on the experimental values of the electric conductivity (electric resistance) of glasses is presented in the handbook [6] for various glass systems.

A substantial number of works is devoted to the theoretical aspects of electrical conductivity, and its relationship with the structure of the liquid and solid states, including glasses.

The electric conductivity of glasses can be measured by using dc and ac currents at low and high temperatures. Methods using ac current are predominately used for measurements — voltage drop, ac current bridge. The latter is the most widely used method for measuring electric conductivity. Information on methods for measuring the electric conductivity of glasses is contained in the monograph [23].

The electric conductivity of glasses depends on the degree of nonequilibrium of the glassy state, i.e., the electric conductivity of hardened glasses is higher than that of the same glasses after annealing. Hardened glasses possess a lower density (more empty spaces), which facilitates movement of cations.

In assessing the influence of the composition of a glass on its electric conductivity, it should be noted that it is affected mainly by the content of alkali oxides. Glass which does not contain alkali oxides (pure quartz glass or glass based on B_2O_3) possesses a very low electric conductivity, which increases rapidly with even very small additions of alkali oxides. Two factors must be taken into account when estimating the effect of the form of the alkaline cation on the electric conductivity: the radius of the cation and the strength with which the cation is bound in the structure of the glass. For example, the ion K^+ is more weakly bound with the

structure than is Na^+, but because of its larger radius K^+ gives rise to a higher resistance during motion. Conversely, the ion Li^+ is smaller than the ion Na^+, but it is more strongly bound in the structure of glass and decreases the electric conductivity compared with the ion Na^+. When two alkali-metal oxides are present simultaneously in glass, for example Na_2O and K_2O (two forms of cations — Na^+ and K^+), the electric conductivity of the glasses decreases compared with that of glasses containing only one alkali oxide (effect of two alkalis). Introducing divalent-metal oxides into glass decreases the electric conductivity. The compounds PbO, BaO, and CaO have an especially large effect. The compounds SiO_2 and B_2O_3 decrease the electric conductivity. Pure borate glasses possess a lower conductivity than similar silicate glasses. When Al_2O_3 is introduced into silicate glasses instead of SiO_2, electric conductivity increases somewhat. The effect of the composition of glass on the electric conductivity is examined in [6, 23].

The electric conductivity of glasses is an activation process, and it increases substantially with temperature (electric resistance decreases correspondingly). At low and high temperatures the electric conductivity and the resistance of glasses vary exponentially with different values of the constant in the exponential equation. The character of the temperature dependence of the electric conductivity (resistance) changes in an anomalous interval. A number of expressions have been suggested for the temperature dependence of the electric conductivity of glasses; these expressions are a systematized in the monograph [23].

The electric conductivity (electric resistance) of melts plays a determining role during electric founding of glasses. The character of the temperature dependence of the resistivity of a glass mass is important. As temperature increases, resistivity decreases; the temperature coefficient of resistance $d\rho_e/dt$ also decreases. The latter means that self-maladjustment occurs during electric founding of glass. This effect is all the stronger, the more the resistivity of the glass changes with temperature.

Figure 4 shows the temperature dependences of the resistivity of the melts of glasses with different compositions [24] and comparative values of $d\rho_e/dt$. As one can see, sheet and container glass as well as lead crystal are characterized by a comparatively weak self-maladjustment, while low-alkali borosilicate glasses have a much higher maladjustment. In the practice of glassmaking, self-maladjustment means that the hot parts, i.e., the parts with higher conductivity, are heated more strongly, while the cooler parts are cooled even more. If the feed electrodes remain under a constant voltage, then a varying current and therefore temperature would result. In this connection, the power supply circuit must be equipped with appropriate regulating devices. The larger the self-maladjustment characteristic of glass, the wider the range of regulation of the voltage of the power supply should be.
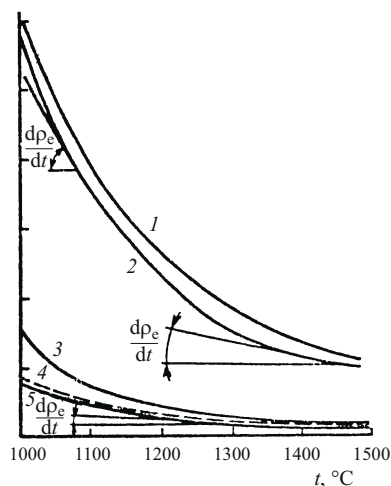

Fig. 4. Temperature dependencies of the resistivity of glasses: *1*, *2*) low-alkali borosilicate glass; *3*) lead crystal; *4*, *5*) sheet and container glass, respectively.

A similar effect is also observed for the effective thermal conductivity of a glass mass, especially at high temperatures. This effect concerns primarily the radiation component of the effective thermal conductivity, i.e., the transparency of the glass mass with respect to thermal radiation (diathermancy). The lower the diathermancy, the worse heat transfer is, so that near and between the electrodes the glass mass becomes overheated. This factor must be taken into account in electric founding of colored glasses, especially glasses with low diathermancy.

Practical questions concerning electric founding of glass are examined in the monographs [23, 24].

Thermal conductivity characterizes the capability of a material to conduct heat in a graded temperature field. As noted above, the transfer processes for heat and matter are similar to one another [2, 3]. But this similarity concerns only low-temperature processes. In this case, the heat flux, by analogy with diffusing particles, is regarded as a flux of quasiparticles — phonons, which arises during thermal vibrations of a group (or system) of atoms (ions) bound with one another. The phonons, propagating in a solid material, are scattered when they encounter one another or lattice defects. In glasses, where atoms (ions) are distributed chaotically, scattering is more significant than in crystals. This explains the low thermal conductivity of glasses.

The true thermal conductivity for silicate glasses varies as a function of composition from 0.6 to 1.34 $W/(m \cdot K)$. The highest value of thermal conductivity is characteristic for quartz glass. As the content of the modifier in the glass increases, the thermal conductivity decreases and all the more, the higher the content of the modifying components. The presence of a correlation between the thermal conductivity and density is supported experimentally: the introduction into glass of heavy-metal oxides (PbO, BaO, and others) decreases the thermal conductivity. The true thermal conduc-

TABLE 1.

Content, %		Average photon mean free path, cm, at temperature, °C			Absorption coefficient k^{-1}, cm^{-1}	Founding regime
Fe$_2$O$_3$	Cr$_2$O$_3$	1000	1200	1400		
0.02	–	5.12	6.40	7.26	10.1	Oxidative
0.10	–	1.82	2.22	2.65	3.30	Reducing
0.20	–	1.26	1.56	1.82	1.99	Oxidative
0.20	–	1.10	1.38	1.82	1.83	Reducing
0.50	–	0.73	0.95	1.03	1.07	Oxidative
0.50	–	0.62	0.77	0.86	0.86	Reducing
–	0.01	5.60	4.82	4.48	–	Oxidative
–	0.10	1.90	1.52	0.97	–	Weakly reducing
–	0.10	2.80	1.70	0.75	–	Strongly reducing

tivity of commercial glasses is $0.72 – 0.9$ W/(m · K). The values of the thermal conductivity for various glasses as well as methods for calculating it are presented in textbooks and learning aids as well as in the handbook [6] and the learning aid [8].

At temperatures up to 200°C heat is transferred in glass predominantly by heat conduction. At higher temperatures the fraction of radiation in heat transfer increases continually and the principles of similarity of transfer phenomenon are not satisfied. The fraction of radiation depends not only on temperature and the absorption coefficient of the glass but also on the thickness of the layer and the geometric parameters of the article. For example, the fraction of radiation in heat transfer for a glass mass in the bath of a glass-making furnace will be much higher than during the formation of articles, especially articles with thin walls.

Thus, the heat transfer process in glass at high temperatures will be characterized by the effective thermal conductivity

$$\lambda_{eff} = \lambda_t + \lambda_{rad} = \lambda_t + 16/3(\sigma_{rad} \, n^2 \, T^3 f),$$

where λ_t is the true thermal conductivity; λ_{rad} is the coefficient of heat transfer by radiation; σ_{rad} is a radiation constant; n is the index of refraction; T is the absolute temperature; and, f is the average free path length of a photon (depends on the type of glass, content of coloring oxides, and temperature).

The average values of free path of a photon for glasses containing Fe$_2$O$_3$ and Cr$_2$O$_3$ are presented in Table 1 (according to data of M. Cherney, L. Hentzel, et al.).

The thermal diffusivity characterizes the rate of change of the temperature of the body in nonstationary thermal processes, for example, when a body with temperature t_1 is placed in a medium with temperature t_2. The thermal conductivity is determined from the relation

$$a = \lambda/c\rho,$$

where λ is the thermal conductivity, c is the specific heat capacity, and ρ is the density.

An important technological characteristic of glass is its diathermancy, i.e. transparency to thermal (infrared) radiation, which is determined by the photon mean free path (see Table 1). The diathermancy of glasses is very important for glassmaking and the formation of glass articles.

The low diathermancy of colored glasses gives rise to substantial temperature gradients on heating and cooling of the glass. This complicates the founding of glass and the formation of glass articles. It was noted above that a low diathermancy has a negative effect on self-maladjustment during electric founding.

Glasses with high diathermancy are heated better during founding, cooled more uniformly, and solidify during formation, thereby increasing the uniformity of glass, increasing the production capacity of the glass-forming equipment, and increasing the quality of the articles.

The technological characteristics associated with diathermancy in glasses, and the factors influencing founding, formation, and annealing, are presented in the reviews [10 – 13].

Interrelationship of transfer phenomena. This interrelationship is obvious, since all transfer phenomena are due to the movement of particles (ions) and transfer all momentum (thermal conductivity is determined by the motion of quasiparticles — phonons). At the same time the phenomenon due to particle motion (diffusion, electricity conduction) are directly related to viscosity as a resistance factor of the medium. For the true thermal conductivity of glasses, this relation is not so obvious since as temperature increases, the fraction of radiation in heat transfer increases rapidly, and heat transfer by radiation plays a determining role for glass-forming melts. A theoretical analysis of the similarity and interrelation of transfer phenomena is given in the monograph [2].

The migration processes of diffusion and electric conduction for cations are of the same nature. The presence of an electric field orders the motion of the cation in the direction of the field. The interrelation of diffusion and electric conduction is expressed by the generalized Nernst – Einstein relation:

$$D = (\alpha n \chi k T)/[N(ze)^2], \qquad (1)$$

where D is the diffusion coefficient, α is a correlation factor, n is the transfer number, χ is the specific electric conductivity, k is Boltzmann's constant, T is the absolute temperature, N is the number of ions per unit volume, z is the valence of a moving ion, and e is the electron charge.

The results of investigations concerning the applicability of this relation for solid glasses are presented in the monograph [25]: the conditions under which the relation (1) holds are discussed and the results of the calculation of the diffusion coefficients using data on the electric conductivity and

Eq. (1) in the temperature range 300 – 1000°C are presented. The investigations of ion diffusion and electric conductivity established that the Nernst – Einstein relation for glasses holds taking account of a definite correlation factor, whose value is independent of the type of glass-forming oxide, but which is sensitive to structural-coordination rearrangement and to a change in the mechanism of the cation motion. The satisfaction of the Nernst – Einstein relation for glasses, taking account of the values of the correlation factors, permits in many cases calculations of the diffusion coefficient on the basis of data on the electric conductivity; this decreases substantially the labor involved in experimental work.

The interrelationship of transfer phenomena and viscosity was first established on the basis of theoretical notions. For diffusion, this interrelationship is expressed by the Einstein – Stokes equation, which relates the diffusion coefficient with the viscosity and radius of the kinetic units and is applicable mainly for the diffusion of colloidal particles or large organic molecules:

$$D = kT/6\pi r\eta, \qquad (2)$$

where $\pi = 3.14$ and r is the radius of the moving particle.

For high-viscosity glass-forming melts the relation between diffusion and viscosity, as obtained from Eq. (2), is not satisfied. This is because the resistance forces of a continuous medium during motion of a colloidal particle with a spherical shape (in a colloidal solution) or large organic molecules are substantially different from the resistance forces of a medium with motion of particles of atomic size.

A series of investigations established that the relation between the migration processes mentioned above (diffusion and electric conduction) and the viscosity is expressed by similar equations

$$\left.\begin{array}{r} D^m\eta = C_1; \\ \chi^n\eta = C_2, \end{array}\right\} \qquad (3)$$

where m, n, C_1, and C_2 are constant coefficients.

Since the temperature dependences of the viscosity, diffusion, and electric conductivity are expressed by similar exponential equations, according to A. I. Frenkel', the coefficients m and n in equations (3) express the ratio of the activation energies of viscous flow E_η, diffusion E_D, and electric conductivity E_χ:

$$m = E_\eta/E_D;$$

$$n = E_\eta/E_\chi.$$

There is a comparatively large number of works on the investigation of the relationship between transfer phenomena silicate melts and glasses.

Data on the interrelationship of the diffusion of gases and the viscosity of glasses are presented in [18, 19]. According to the data in [19], the diffusion of water in glasses is related with their viscosity by the following equation:

$$-\log D_{H_2O} = \log \eta + 5.82 - 4100T, \qquad (4)$$

where η is the viscosity, dPa · sec, and T is the absolute temperature, K.

The diffusion coefficients of H_2O for silicate glasses with different compositions at temperature 1000 – 1400°C, calculated according to equation (4), satisfactorily agree with experimental data. In the review [19] of gas diffusion in glasses, the diffusion mobility of OH groups in fused technical glasses exhibits a relation with the viscosity according to the equation

$$-\log D_{OH} = K - \log \eta,$$

where K is a constant.

The authors explained all of the experimental data on D_{OH} assuming that water diffuses in silicate melts by means of the motion of autonomous hydroxyl groups with breaking of silicon-oxygen bonds in the groups $\equiv Si - O - H$.

Numerous experiments for glasses with different compositions confirm that the relation (3) for the viscosity and electric conductivity is satisfied. At the same time, investigations of a series of commercial and experimental glasses in a wide temperature interval (500 – 1400°C) have established that the values of the constants n and C are different for the high temperature region (fused state) and for an anomalous temperature range (viscosity $10^7 - 10^{13}$ Pa · sec).

Similarity (dimensionless) numbers are widely used in investigations, modeling, and calculations of technological processes and equipment. These numbers are determined by the ratios of the properties of materials and the characteristics of a process, including transfer phenomena (Re, Pr, Pe, Nu, and others):

$$\left.\begin{array}{r} Re = wd/\nu; \\ Pr_D = \nu/D; \\ Pr_\lambda = \nu/a; \\ Nu_D = \beta d/D; \\ Nu_\lambda = ad/\lambda, \end{array}\right\} \qquad (5)$$

where Re is Reynolds number; Pr_D and Pr_λ are the diffusion and thermal Prandtl numbers; Nu_D and Nu_λ are the diffusion and thermal Nusselt numbers; w is the flow rate of the liquid; d is the characteristic size; ν is the kinematic viscosity; D is the diffusion coefficient; a is the thermal diffusivity; β is the mass transfer coefficient; and, λ is the thermal conductivity.

The main parameters of a moving liquid are the Reynolds number and Prandtl's diffusion number, which characterize, respectively, the regime of motion and the physical-chemical properties of the liquid. The motion of a glass mass in glass-making furnaces is characterized by low Reynolds numbers, and in this connection the value of

Prandtl's diffusion number plays a greater role. For glass melts the Prandtl number can be $10^8 - 10^{10}$, which underscores certain features of the diffusion process in high-viscosity melts.

For the dissolution of quartz grains or dye particles in a high-viscosity glass-forming melt, the conditions for dissolution can be expressed by the equation

$$Nu = 2 + Re^{a^*} Pr^{b^*},$$

where a^* and b^* are coefficients.

Here the Nusselt number characterizes mass transfer and the Reynolds and Prandtl numbers characterize, respectively, the regime of motion of the flux with respect to the dissolving particle and the physical-chemical properties of the flux (5). Setting certain boundary conditions, it is possible to estimate the thickness of the diffusion layer and the rate of dissolution as a function of the particle size and therefore to create the conditions required to intensify the process.

There is also experience in commercial application of the interrelationship of transfer phenomena. Specifically, the interaction of viscosity and electric conductivity can be used to monitor the viscosity in the feed channel during production of glass containerware. Here, the daily fluctuations of the electric resistance and viscosity during ordinary operation of machines can be monitored. The viscosity fluctuations are studied with respect to the average daily value, and a picture is thereby created of the viscous regime of the feeder. The values of the resistance are converted to viscosity in accordance with the relation (3) for the viscosity and electric conductivity.

The advantages of such monitoring of the viscosity are the use of small stationary sensors and the possibility of on-line control of the technological process.

Analysis of the technological processes and increasing the efficiency of glass production are directly related with the study of the properties and characteristics of glasses, including transfer phenomena, in application to concrete technological conditions of the production process.

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